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Synthesis of Platinum Nanowire Networks Using a Soft Template

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Abstract: *Platinum nanowire networks have been synthesized by reduction of a platinum complex using sodium borohydride in the presence of a soft template formed by cetyltrimethylammonium bromide in a two-phase water-chloroform system. The interconnected nanowires possess the highest surface area and electroactive surface area reported for unsupported platinum nanomaterials. Synthetic control over the network was achieved by varying the stirring rate and reagent concentrations. A mechanism of formation of the metal nanowire networks is proposed based on confined metal growth within a network of swollen inverse wormlike micelles. Expected applications include catalysis for fuel cells and solar water splitting devices.*

Keywords: Platinum, Nanowires, Catalysis, Nanomaterials

1. Introduction

Herein we describe a novel method for the synthesis of uniform platinum nanowire networks by a modified phase transfer method in an oil/water emulsion system. Nanostructured platinum is important in many technical applications, including as an electrocatalyst in proton exchange membrane fuel cells and as catalysts in many reactions including solar water-splitting devices. Our synthesis takes advantage of the formation of a worm-like network of inverse bi-continuous micelles of cetyltrimethylammonium bromide (CTAB) in an oil/chloroform emulsion system which serves as a soft template for the reduction of an aqueous platinum salt. The obtained platinum metal retains the structure of the templating agent in the form of uniform platinum nanowire networks. Synthetic control is achieved by simply varying the stirring rate, and reagent concentrations. The soft template approach is superior to syntheses that use hard templates such as silica which are difficult to produce and require etching of the substrate with environmentally hazardous chemicals such as hydrofluoric acid.

2. Experimental (or Theoretical)

A typical synthesis was performed in two steps, a phase transfer step and a platinum reduction step. In the phase transfer step an aqueous solution of Potassium Tetrachloroplatinate (K_2PtCl_4) was combined with a solution of CTAB in chloroform and stirred for 10 minutes. The initially orange water phase becomes clear and the chloroform phase becomes orange veryfying the complete transfer of platinum complex. Nanopure water was added to the chloroform solution (80% by volume) and stirred at 1000 RPM's followed by the addition of an aqueous solution of Sodium Borohydride (NaBH4) (10% by volume). The reaction was allowed to proceed with stirring for 30 minutes.

3. Results and discussion

The presence of the interconnected inverse micelle network is studied by the method developed by the Evans' group who suggests that the interconnectivity of the water channels within a swollen micelle network can be measured by electrical conductivity. Indeed our system shows increased electrical conductivity at high CTAB concentrations suggesting a large interconnected network through the continuous water channels and low conductivity at low CTAB concentrations suggesting separated spherical micelles. Characterization of the obtained nanowires by TEM and SEM imaging revealed uniform networks with an average cross-sectional diameter of 2.2 nm by measurement of 100 randomly selected wire segments. A surface area of 53 ± 1 m2/g was determined from the nitrogen adsorbtion isotherms using the Bruner Emmet Teller (BET) method. The pore size distribution was measured to be 2-10 nm by the Barrett Joyner Halenda (BJH) method. The electroactive surface area was measured to be 32.4 ± 3.6 m2/g from a carbon monoxide stripping voltamagram. An X-Ray diffraction spectrum of the sample revealed that the materials have a face centered cubic (FCC) crystalline structure. Variation of the CTAB concentration led to synthetic control over the nanomaterial structure giving separated particles at low CTAB concentrations and extended nanowire networks at high CTAB concentrations both of which are consistent with the electrical conductivity measurements. The stirring rate also allows some control over the network. Without stirring the reaction produced very few nanowires with very large knobs at the intersections. Stirring at a high rate resulted in the formation of uniform nanowires without knobs. The improvement in uniformity and reduced knob size is likely due to more efficient mass transfer of Sodium Borohydride as a result of creating more interfacial surface areas at high speeds. The diameter of the nanowire network can be controlled to some extent by simply varying the concentration of platinum salt as evidenced in the TEM and SEM images.

4. Conclusions

In conclusion, polycrystalline platinum nanowire networks with uniform wire diameters were synthesized by using a network of wormlike micelles as a soft template for metal growth. This study provides a clear demonstration of the use of soft micellar networks as templates for the successful synthesis of interconnecting metal nanowires that accurately reflect the micellar network structure. The structural features of these platinum networks can be controlled to some degree, including the diameter of the wires and the size of knobs formed at intersecting points. A possible formation mechanism based on soft templating by the micellar networks contained in chloroform droplets is proposed. The platinum nanowire network has the highest surface area and electroactive surface area reported for unsupported platinum nanomaterials and therefore is expected to have potential applications in catalysis and electrocatalysis. This work opens new opportunities for employing other soft templates to realize shape control over metallic nanomaterials.

References

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